## ELECTRO-  AND  PLASMA CHEMICAL  TECHNOLOGIES

# On Reasons for Varied Reversibility of Different Kinds of Nickel Oxide Electrodes in Alkaline-Zincate Electrolytes

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**Abstract**—Significant difference between the working capacities in zincate electrolytes of reversible nickel oxide electrodes of two types, lamellar with a graphite additive and metal-ceramic, was noted. It was demonstrated that the electrochemical reversibility of the active substance of nickel oxide electrodes is strongly impaired in the simultaneous presence of the carbon (graphite) component and oxygen in the reacting electrodes and zincate in the electrolyte. In operation of electrodes of this kind in alkaline nickel-zinc batteries, the oxygen-involving process is of side (parallel) nature.

The concept of developing high energy-storage-capacity nickel-zinc batteries by combining the practically used nickel oxide electrodes (NOEs) from alkaline batteries of nickel-cadmium (NC) and nickel-iron (NI) systems with reversible zinc electrodes from silver-zinc batteries has long attracted researchers' attention [1]. The electrochemical system of a battery of this kind, Zn|KOH, K$_2$[Zn(OH)$_4$]|NiOOH has the following charge-discharge reaction

$$ZnO + 2\,Ni(OH)_2 \underset{\text{Disharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Zn + 2\,NiOOH + H_2O.$$
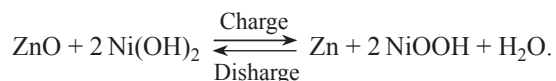
The battery must have a discharge voltage of 1.7–1.5 V, i.e., a voltage 20–25% higher than that of NC and NI batteries. Attempts to fabricate batteries of this kind with domestic NOEs of lamellar design from alkaline batteries, which have the form of a compacted active paste composed of a mixture of a Ni(OH)$_2$ powder with a conducting graphite additive (~17 wt %), binder, and certain improving additives, have failed. The discharge curve of nickel oxide electrodes became of two-plateau type in an alkaline-zincate electrolyte, with a long second plateau by approximately 0.4 V lower than the NOE potential in discharge of alkaline NC and NI batteries having a stable discharge potential in operation (Fig. 1).

## EXPERIMENTAL

We used in test NZ batteries a combination of a single nickel oxide electrode, a lamellar or metal-ceramic (MC) capacity limiter fabricated by impregnation of a highly porous sintered nickel base [1], and two zinc powder electrodes of the reversible type with a hydrated cellulose separator. In the control variant, we used test nickel-cadmium batteries with one lamellar NOE and two cadmium powder electrodes. The electrolyte was composed of 7 M of KOH + 5 g L$^{-1}$ LiOH·H$_2$O. The discharge current density was 7.5 mA cm$^{-2}$.

The commonly accepted concept is that electrochemical processes occur in NOEs by the solid-phase mechanism as a result of proton migration [2] with a successive transformation

$$NiOOH + H^+ + e \rightleftharpoons Ni(OH)_2, \; E^0 = +0.49 \text{ V}. \quad (1)$$

In the course of operation, the electrolyte of NZ batteries is permanently being saturated with zinc (zincate) ions [Zn(OH)$_4$]$^{2-}$. The anodic oxidation of zinc electrodes is accompanied by the formation of pseudo-saturated zincate solutions [1, 3]. For example, the concentration of zinc ions in the alkaline electrolyte increased

to 53 g L$^{-1}$ during the first seven operation cycles of test NZ batteries, and was 59 g L$^{-1}$ (in terms of Zn$^{2+}$) after the 22nd cycle.

In operation, nickel-zinc batteries with lamellar NOEs rather rapidly lost their working capacity (determined by the duration of the upper discharge plateau with a voltage exceeding 1.5 V) (Fig. 1); the duration of the second plateau with a voltage of 1.25–1.1 V increased with the number of charge-discharge cycles.

A fundamentally different working capacity in zincate electrolytes was observed for metal-ceramic NOEs. These electrodes had only a single discharge plateau and the capacity hardly decreased in prolonged cycling in NZ batteries at the working potential (Figs. 1 and 2). The mechanism of the so-called "poisoning" of the NOE by zincate remains incompletely understood. Reasons for various effects of zincate on the charge-discharge processes in NOEs of different designs were examined in our present study.

Electrochemical reactions occur on NOEs with transformation of the active substance in parallel with a process involving molecular oxygen (current efficiency of about 70% for a lamellar NOE [1]). Experiments with NOEs of different designs demonstrated that effect of zincate on these electrodes must be manifested via a reaction with oxygen, whose specific features in zincate electrolytes have been little studied.

The carbon (graphite) surface of the lamellar electrodes under study exhibits pronounced adsorption and chemical-catalytic properties [4, 5], with joint adsorption of oxygen molecules and zincate ions [Zn(OH)$_4$]$^{2-}$ (ZnO$_2$$^{2-}$·2H$_2$O) observed on this surface.

The carbon-based oxygen electrode is, in alkaline-zincate electrolytes, a multiple-electrode system, oxygen O$_2$–carbon (C)–zincate [Zn(OH)$_4$]$^{2-}$, whose components can react with each other to give a new electrochemical system.

The quantity of electricity released by lamellar electrodes in a zincate electrolyte in the second discharge stage cannot be accounted for by the cathodic reduction of adsorbed oxygen in NOE pores [6] (calculated with the electrochemical equivalent, this quantity would be about 0.2 g per gram of graphite). All this suggested that molecular oxygen is converted within a microporous electrode in an alkaline-zincate electrolyte to a product that exhibits a cathodic activity and reacts in a single stage, but with a less positive discharge potential
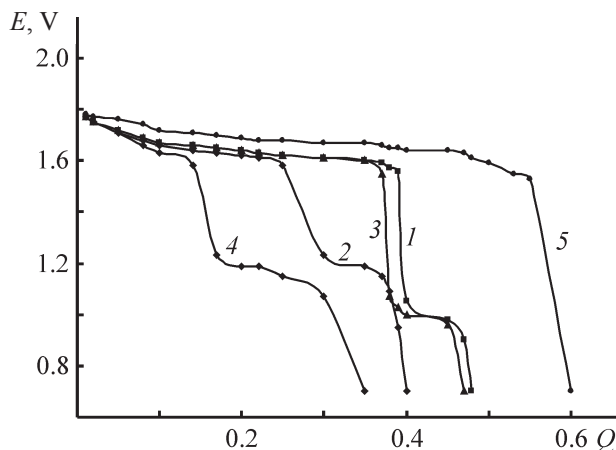


**Fig. 1.** Discharge curves of reversible lamellar NOEs in a 7 M KOH solution at 20°C. $J^{discharge}$ = 7.5 mA cm$^{-2}$ in (*1, 2*) 3rd and (*3, 4*) 19th cycle. Battery: (*1, 3*) NC, (*2, 4*) NZ, and (*5*) NZ with MC NOE. (*E*) Voltage and (*Q*) quantity of electricity.
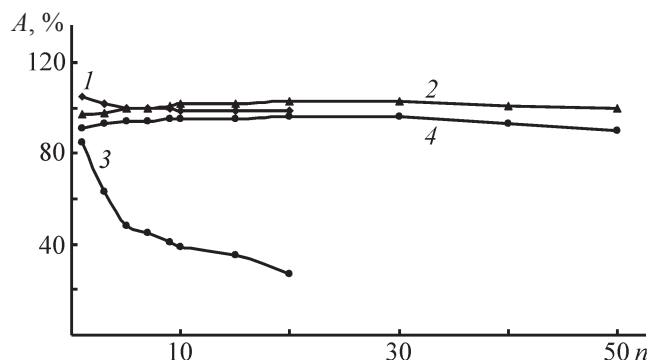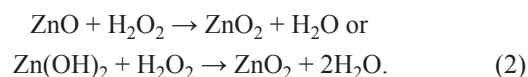


**Fig. 2.** Variation of the relative capacity *A* of NOEs of various types in NC and NZ batteries in cycling. (*n*) Number of cycles. Electrodes: in NC batteries: (*1*) lamellar and (*2*) MC NOE; in NZ batteries: (*3*) lamellar and (*4*) MC NOE.

as compared with the active substance of the NOE. A possible product of this kind, formed as a result of chemical-catalytic transformations on the graphite surface, is zinc peroxide ZnO$_2$.

It follows from the Pourbaix diagram for zinc [7] that ZnO$_2$ can be formed in the pH range under study at $E \geq +0.35$ V relative to the standard hydrogen electrode (s.h.e.) (or +1.57 V relative to zinc).

Peroxide compounds of zinc were obtained in [8] via reaction of zinc oxide or hydroxide with aqueous solutions of hydrogen peroxide by the following equations
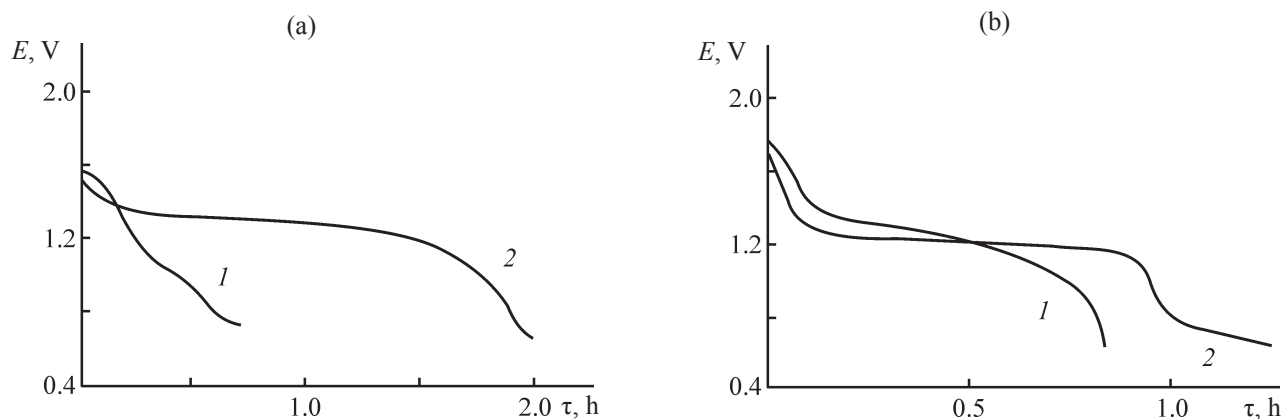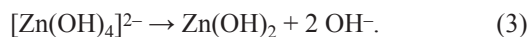
$$ZnO + H_2O_2 \rightarrow ZnO_2 + H_2O \text{ or}$$
$$Zn(OH)_2 + H_2O_2 \rightarrow ZnO_2 + 2H_2O. \quad (2)$$

**Fig. 3.** Discharge curves measured upon treatment with a 10% hydrogen peroxide solution of (a) lamellar and (b) MC NOE. $J_{discharge} =$ 3 mA cm$^{-2}$. ($E$) Voltage and ($\tau$) time. Battery: (*1*) NC and (*2*) NZ.
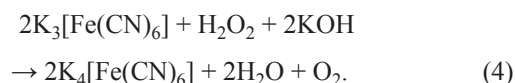
In prolonged operation of NZ batteries, solid particles of zinc oxide (hydroxide) precipitate in NOE pores from an electrolyte pseudo-supersaturated with zincate [1]:

$$[Zn(OH)_4]^{2-} \rightarrow Zn(OH)_2 + 2\,OH^-. \quad (3)$$

In an experiment, NOEs subjected to a deep discharge (until hydrogen evolution onset) were removed from test batteries, the excess of the alkali was removed with a filter paper, and the electrodes were placed in 100 mL of a 10% solution of hydrogen peroxide for 60 min. Then, dried with filter paper, the electrodes from NC batteries were submerged in a 7 M KOH solution (electrodes from NZ batteries), and those from NZ batteries, in a  M KOH solution + 46 g L$^{-1}$ Zn$^{2+}$. On being kept there for 24 h, the electrodes were assembled into the test batteries, which were filled with an alkaline or a zincate electrolyte and discharged with a current of 100 mA.

The lamellar nickel oxide electrodes of test NZ batteries (Fig. 3a) had the longest plateau with a potential of 1.5–1.2 V (relative to a zinc reference electrode) on the discharge curve. A shorter duration was observed for the gradually sloping discharge plateau of MC NOE NZ batteries (Fig. 3b). The discharge curves of NOEs operated in a purely alkaline electrolyte had no pronounced gradually sloping portions, with the discharge duration being about 0.5 h.

In an alkaline electrolyte, hydrogen peroxide is qualitatively and quantitatively determined by using the reaction of catalytic decomposition of H$_2$O$_2$ to give oxygen [9]:

$$2K_3[Fe(CN)_6] + H_2O_2 + 2KOH$$
$$\rightarrow 2K_4[Fe(CN)_6] + 2H_2O + O_2. \quad (4)$$

On being fully charged, the test batteries were disassembled, the NOEs were placed in vessels with gas-collecting burettes, filled with, respectively, alkaline and zincate electrolytes. After the control volume of oxygen released in 15 min was determined, 2 cm$^3$ of a saturated K$_3$[Fe(CN)$_6$] solution was introduced in each electrolyte and the volume of gas released in the following 15 min was measured (see table).

For the lamellar NOE, we observed a nearly 1.5-fold increase in the volume of released oxygen upon introduction of K$_3$[Fe(CN)$_6$], which may indicate that hydrogen peroxide is present within pores of electrodes of this kind, whereas for the MC NOE, the gas volume changed only slightly.

According to [4, 10], formation of hydrogen peroxide in alkaline solutions in an anodic process on graphite is unlikely, it was not observed by the method of a rotating disk electrode with a ring. The process of oxygen evolution on graphite, accompanied by a high overvoltage, occurs at potentials more positive than +1.0 V. On a nickel electrode, the oxygen evolution process occurs at low anodic current densities with a low overvoltage, without the stage of hydrogen peroxide formation [11, 12], via the decomposition of higher nickel oxides (NiO$_2$, Ni$_2$O$_4$).

Hydrogen peroxide can be probably formed as a result of a cathodic reduction of molecular oxygen always present in large amounts within pores of charged NOEs. Even in the idle state, the active substance is self-

Volume of oxygen released during 15 min after full NOE charging

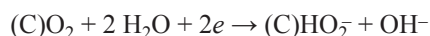| Electrolyte | Volume of released oxygen, cm³ | | | |
|---|---|---|---|---|
| | Lamellar NOE from NZ battery | Lamellar NOE from NC battery | MC NOE from NZ battery | MC NOE from NC battery |
| Alkaline or zincate | 1.4 | 1.7 | 0.6 | 0.5 |
| With addition of 2 mL of $K_3[Fe(CN)_6]$ | 2.0 | 2.2 | 0.7 | 0.55 |

discharged with evolution of oxygen.

Polarization curves measure on the pyrographite electrode in an alkaline medium have well-pronounced limiting-current plateaus [4]. In the range of the first-wave potentials, from +0.8 to +0.3 V, molecular oxygen is reduced, without rupture of the O–O bond, to hydrogen peroxide, which is a stable reaction product in a wide range of potentials [4, 10].

A study of the mechanism of electroreduction of molecular oxygen on nickel [12] by the method of a rotating ring-disk electrode and by ellipsometry demonstrated that the oxidation state of nickel strongly affects the process rate. The sharp acceleration of the cathodic reactions of oxygen and hydrogen peroxide reduction on an electrochemically oxidized nickel electrode was attributed by the authors of [12] to the effect of adsorbed oxygen and nickel oxide phases. At potentials more positive than +0.3 V, solid oxide layers are formed on the surface of nickel. It is difficult to electrochemically reduce oxygen adsorbed on the nickel surface at a potential of +0.5 V in the range of potentials at which its cathodic reduction occurs.
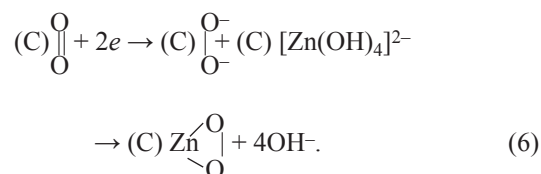
The data of [4, 5, 10, 12] point to differences between the mechanisms by which molecular oxygen is cathodically reduced in NOEs of various types. In the MC NOE, the formation of hydrogen peroxide by the cathodic reaction of oxygen reduction is strongly hindered at its working potentials (+0.5–+0.3 V). In the lamellar NOE, oxygen formed in decomposition of higher nickel oxides is adsorbed on the graphite surface and can be cathodically reduced in the first stage to hydrogen peroxide.

The intraelectrode transformations of oxygen on the carbon electrode in a zincate electrolyte can be conditionally described by the sequence

$$(C)O_2 + 2 H_2O + 2e \rightarrow (C)HO_2^- + OH^-$$

$$\rightleftharpoons (C)O_2^{2-} + H_2O. \tag{5}$$

An indirect evidence that zinc peroxide is formed is provided by the data on the electroreduction of oxygen, on a ring-disk in KOH solutions with addition of $Ba^{2+}$ and $Ca^{2+}$ ions, reported by Tarasevich [4, 12]. With increasing concentration of specifically adsorbed $Ba^{2+}$ and $Ca^{2+}$ ions, a decrease in the amount of hydrogen peroxide at the ring was observed. In the authors' opinion, the presence of the above-mentioned adsorbed cations makes stronger the binding of chemisorbed oxygen to the electrode surface, which formally corresponds to the possible formation of compounds of the $BaO_2$ and $CaO_2$ type on the surface.

Oxygen ion molecules $O_2^{2-}$ are unstable, their bonding energy being comparatively low (about $-200$ kJ mol$^{-1}$) [13]. In a zincate solution, catalytic processes leading to stabilization of oxygen ion molecules by zincate ions to give stable zinc peroxide $ZnO_2$ with high formation energy ($\Delta H_{form} = -350$ kJ mol$^{-1}$ [13]) on the carbon surface. Stages of this process can be conditionally described by the sequence

$$(C)\overset{O}{\underset{O}{\|}} + 2e \rightarrow (C)\overset{O-}{\underset{O-}{|}} + (C)\,[Zn(OH)_4]^{2-}$$

$$\rightarrow (C)\,Zn\overset{O}{\underset{O}{<}}| + 4OH^-. \tag{6}$$

Zinc peroxide poorly soluble in the zincate electrolyte is chemisorbed on the carbon surface of electrode pores, to be cathodically reduced there

$$(C)\,ZnO_2 + 2\,e \rightarrow ZnO_2^{2-} \tag{7}$$

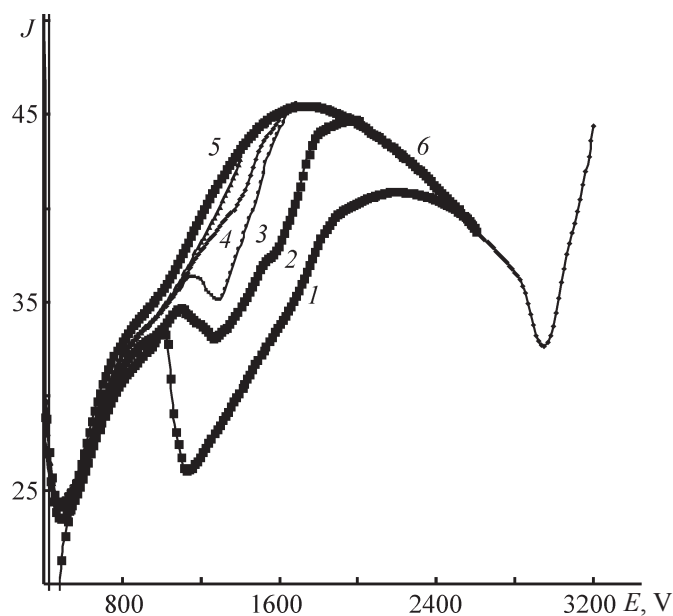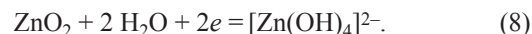at potentials substantially more positive than the NiOOH reduction potential (Fig. 1).

**Fig. 4.** Cyclic anodic polarization curves in the transpassive region for a zinc electrode in 7 M KOH solution. Potential sweep rate 4 mV s$^{-1}$. ($J$) Current density and ($E$) anodic polarization. Potential variation range (mV): (*1*) 380–2600, (*2*) 380–2000, (*3*) 380–1800, (*4*) 1600, (*5*) 380–1400, and (*6*) anodic curve 380–3200 (forward run).

To find the region in which $ZnO_2$ starts to be formed, we carried out the following experiments. A zinc electrode was cycled in the potentiodynamic mode in the potential range $E_c$–$E_a$, where $E_c$ = 0.380 V (relative to zinc) is the cathodic end of the cycling range, and the potential $E_a$ is varied in each subsequent set of experiments (Fig. 4). $E_a$ was +3.2 V in the first set, +3.0 V in the second, etc.; with the potential lowered to $E_a$ + 1.4 V at which potential no $ZnO_2$ reduction wave is observed. In the reverse run of the anodic polarization curve, the anodic current will be the difference between the anodic current with migration of $Zn^+$ ions and the cathodic current of $ZnO_2$ reduction.

In oxidation of zinc at anodic potentials lower than +1.5 V, there is no wave of $ZnO_2$ reduction in the potentiodynamic curves and the yellow color of the electrode surface disappears, which indicates that there is no $ZnO_2$.

Attention should be given to the fact that the enthalpies of formation, $\Delta H^o$, of zinc peroxide and zinc oxide nearly coincide: $\Delta H^o$ = –350 kJ mol$^{-1}$ for $ZnO_2$ and –350.8 kJ mol$^{-1}$ for ZnO [7, 13]. The entropies of ZnO and $ZnO_2$ must differ, with $ZnO_2$ having a higher entropy than ZnO ($S_{ZnO}$ = 44 J mol$^{-1}$ K$^{-1}$ [13]) because

of the increased complexity of the molecule of the former. We could not fins values of entropy for $ZnO_2$. An analysis of the entropies of oxides of metals in different oxidation states demonstrated [13] that the entropy of higher oxides is approximately 1.2–1.4 times that of lower oxides. Based on this circumstance, we take the entropy to be 62 J mol$^{-1}$ K$^{-1}$ at a temperature of 298 K. Then, we can estimate the equilibrium potential of $ZnO_2$ formation on the basis of the reaction

$$ZnO_2 + 2\,H_2O + 2e = [Zn(OH)_4]^{2-}. \qquad (8)$$

The value of $\Delta G^o$ is –59 kJ mol$^{-1}$. From the dependence $\Delta G = -zFE$, we find the equilibrium potential of reaction (8): $E_{eq}$ = +0.305 V (s.h.e.) or 1.53 V (relative to zinc), which nearly coincides with the onset potentials of $ZnO_2$ formation and reduction.

At the beginning of operation of NZ batteries, when the zincate content of the electrolyte is low, the main current-yielding process in a lamellar NOE is by reaction (8) involving the active substance. In the course of discharge of the batteries, the concentration of zincate ions in the alkaline electrolyte substantially grows and the oxygen-involving process occurring at the surface of graphite particles will be accompanied by the formation of electrochemically less active "ballast" zinc peroxide. This substance is chemisorbed and shields active NOE particles, which gradually diminishes the usable capacity of the electrode. With increasing zincate content of the electrolyte, the rate of $ZnO_2$ formation will become higher.

Zinc peroxide has a higher thermal stability and is less subject to the influence of moisture, compared with peroxides of alkali and alkaline-earth metals, which enables its use in pyrotechnics, medicine, food industry, and wastewater purification. The chemical (electrochemical) stability is imparted to zinc peroxide in an alkaline-zincate electrolyte by the potential of the reversible electrochemical process (2) involving the active substance of NOE, imposed on the electrode. During the idle and low-discharge periods, the NOE potential will be in the range from +0.6 to +0.35 V (s.h.e.) (+1.8 to + 1.55 V relative to zinc), i.e., in the range of $ZnO_2$ formation.

The larger the amount of zinc peroxide formed in cycling of NZ batteries, the lower the usable capacity of a lamellar NOE. In the end, the limiting current density for electrochemical conversion of the active substance

is reached in discharge, which leads to an increase in the electrode polarization to the $ZnO_2$ reacting potential, with transition of the NOE discharge process to the second potential plateau.

The shielding of active particles, nickel oxides, by the zinc peroxide being formed is one of reasons for the so-called zincate "poisoning" of a lamellar NOE with an electrically conducting graphite additive. However, the cathodic reaction of zinc peroxide by equation (8) to give a soluble product fails to restore the initial capacity of electrodes of this kind. It is not improbable that the cathodic reduction of zinc peroxide in deep zones of the active substance of the electrode proceeds to give an oxide phase

$$ZnO_2 + H_2O + 2\,e \rightarrow ZnO + 2\,OH^-. \tag{9}$$

Calculations made for reaction (9) yielded the following values: $\Delta G^o = -62.9$ kJ mol$^{-1}$ and $E_{eq} = +0.326$ V (s.h.e.) or 1.545 V relative to zinc, which only slightly differs from the onset potentials of $ZnO_2$ formation and reduction by reaction (8). Here, it is necessary to take into account the slowness of the chemical stage of dissolution of the cathodic products formed in the electrochemical reaction involving zinc peroxide, which depends on the concentration of zincate dissolved in the alkaline electrolyte.

$$ZnO + 2\,OH^- + 2\,H_2O \rightarrow [Zn(OH)_4]^{2-}. \tag{10}$$
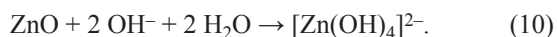
The reactivity of the oxide film being formed is low and it can also shield active particles or favor incorporation of zinc ions into these particles [2, 6].

Another reason why the capacity of the lamellar NOE decreases in zincate electrolytes is that the charging process of zincate-poisoned NOE is hindered [6]. In the subsequent charging, a part of the active substance at outer parts of a discharged zincate-poisoned electrode is additionally oxidized, which preserves a small part of the upper potential plateau in the NOE discharge curve (Fig. 1).

Studies of various kinds of NOE in an alkaline electrolyte demonstrated that the electrochemical reversibility of their active substance is strongly impaired in the simultaneous presence of the catalytically active carbon (graphite) component and oxygen in the reacting electrodes and of zincate in the electrolyte. Elimination of zincate from the electrolyte (in NC batteries) enables

operation of the lamellar NOE at its ordinary (working) potentials of reaction of nickel hydroxides, whose discharge curve is more stable (Fig. 1). Metal-ceramic NOEs containing no graphite component are also hardly poisoned by the zincate electrolyte and can be recommended for fabrication of high-energy-capacity NZ batteries capable of prolonged operation in various modes.

## CONCLUSIONS

(1) A significant difference was observed between the working capacities in zincate electrolytes of reversible nickel oxide electrodes of two types, lamellar with a graphite additive and metal-ceramic. The electrodes of the first type were hardly operable, had a discharge curve rapidly becoming of the two-plateau type in cycling, and rapidly lost their working capacity. The metal-ceramic electrodes had a stable capacity in prolonged operation in nickel-zinc batteries.

(2) The zincate poisoning of lamellar nickel oxide electrodes is due to the catalytic transformation of the originally formed hydrogen peroxide on graphite particles to cathodically active zinc peroxide with a lower discharge potential, which mechanically shields, as also do its discharge products, particles of the active substance. In metal-ceramic electrodes, the formation of hydrogen peroxide is strongly hindered, which precludes formation of the «ballast» zinc peroxide.

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